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Nuclear Chemistry

Change in the Decay Constant of ^{99m}Tc in BaTiO_3 by the Ferroelectric Transition. M. Nishi and S. Shimizu. *Phys. Rev. B*, 5, 3218 (1972).—The BaTiO_3 ceramic samples were prepared by sintering mixtures of BaCO_3 , TiO_2 , and $\text{Na}^{99m}\text{TcO}_4$ at 1400°C . In these samples ^{99m}Tc atoms are located at the lattice site of the Ti atoms in the BaTiO_3 crystals, where an intense internal electric field acts. The relative change in the decay rate of the 2.17-keV $E3$ isomeric transition of ^{99m}Tc embedded in BaTiO_3 in the ferroelectric state (at room temperature) and the paraelectric state (at 170°C) was measured. The result obtained is $\lambda[\text{BaTi}(^{99m}\text{Tc})\text{O}_3 \text{ in paraelectric state}] - \lambda[\text{BaTi}(^{99m}\text{Tc})\text{O}_3 \text{ in ferroelectric state}] = (2.6 \pm 0.4) \times 10^{-3} \lambda[\text{BaTi}(^{99m}\text{Tc})\text{O}_3 \text{ in ferroelectric state}]$. Statistics and errors of the measurement are discussed. It is reasonable to conclude that the main contribution to the observed effect comes from a change in the $4p$ electron density near the nucleus caused by the influence of the internal electric field in BaTiO_3 .

K-Shell Internal Ionization Accompanying Beta Decay. Y. Isozumi and S. Shimizu. *Phys. Rev. C*, 4, 522 (1971).—Internal ionization in the K shell during nuclear β decay has been studied experimentally as well as theoretically. The subsequent K x rays were measured in coincidence with emitted electrons for various segments of the β spectra of ^{147}Pm and ^{63}Ni , using 4π detection geometry for these electrons; the sources were mounted in the electron detectors. The energy-dependent ionization probability $P_K(E_\beta^0)$ was measured as a function of E_β^0 , where the parameter E_β^0 is defined as a sum of energies of the β particle and emitted K electron plus the K -shell binding energy of the daughter atom. This energy-dependent and the simultaneously measured total ionization probabilities have been found to be in fairly good agreement with theoretical values calculated by the theory developed based on a relativistic one-step treatment of electron shakeoff. From this result it has been established that electron shakeoff is the predominant mechanism even for electrons (β particles and K electrons) emitted with very low energies. As to the total ionization probability, it is pointed out that the theoretical values calculated by the simple wave-function-overlap theory using self-consistent-field wave functions should be improved by multiplying by a correction factor, a function of B_K and E_0 , where B_K is the K -shell binding energy of the daughter atom and E_0 is the ordinary maximum kinetic energy of β rays. The theoretical treatment of the phenomenon and future fruitful experiments to be hoped for are also discussed.

Nuclear Excitation by Positron Annihilation. T. Mukoyama and S. Shimizu. *Phys. Rev. C*, 5, 95 (1972).—A new mode of positron annihilation has been investigated

experimentally. In this annihilation process without emission of radiation, the excess energy liberated is given to the nucleus involved. The experimental evidence for this process was established by observing the conversion electrons from $^{115\text{m}}\text{In}$, first excited level (335 keV, $\frac{1}{2}^-$), after irradiation of natural indium foils by positrons from the β^+ decay of ^{22}Na . Using the experimental data obtained, we have attempted to evaluate the cross section for positrons having just the energy corresponding to that necessary to excite ^{115}In from the ground state to an excited level which may decay to the isomeric level concerned. The experimental value of the cross section is found to be $\sim 10^{-24} \text{ cm}^2$, while the theoretical value estimated by Present and Chen is $\sim 10^{-26} \text{ cm}^2$. Possible reasons for this difference are discussed.

Effect of Pressure on the Decay Constant of $^{99\text{m}}\text{Tc}$. H. Mazaki, T. Nagatomo and S. Shimizu. *Phys. Rev. C*, 5, 1718 (1972).—An experimental investigation of the influence of high hydrostatic pressure on the decay constant of $^{99\text{m}}\text{Tc}$ has been performed. By the use of a multianvil high-pressure apparatus, a carrier-free source of $^{99\text{m}}\text{Tc}$ was compressed at a pressure of 100 kbar. The observed decay rate of the compressed $^{99\text{m}}\text{Tc}$ source was compared with that of a standard $^{99\text{m}}\text{Tc}$ source in the normal uncompressed state. The fractional increase in the decay constant, $\Delta\lambda/\lambda$, of the compressed $^{99\text{m}}\text{Tc}$ under that pressure was found to be $(4.6 \pm 2.3) \times 10^{-4}$. Our result agrees with that observed by Bainbridge, $\Delta\lambda/\lambda = (2.3 \pm 0.5) \times 10^{-4}$, to within a factor of about 2. Comparison with theoretical studies by other workers is also discussed.

Summing-Energy Spectrum of the Beta Particles Plus Emitted K Electrons in the K-Shell Internal Ionization Accompanying the Beta Decay of ^{63}Ni . T. Kitahara, Y. Isozumi and S. Shimizu. *Phys. Rev. C*, 5, 1810 (1972).—Through a new type of experiment to obtain information on the K-shell internal ionization in β decay, the summing-energy spectrum of electrons (β particles plus emitted K-shell electrons) in coincidence with emitted K x rays in the β decay of ^{63}Ni has been observed directly using two proportional counters. The procedure and results are discussed.

Dilute ^{57}Co Mössbauer Study on a Ferromagnetic Ni-Cu Alloy near the Transition Temperature. S. Nasu, Y. Murakami and R. Katano. *Phys. Letters*, 36A, 117 (1971).—Temperature dependence of the ^{57}Fe Mössbauer spectra in a ferromagnetic $\text{Ni}_{0.69}\text{Cu}_{0.31}$ alloy was measured. The analysis of hyperfine field distributions in the vicinity of the transition temperature provides a clue to elucidate the clustering and/or concentration fluctuation in this alloy system.

Possible Evidence for a Contribution from Direct Collisions in K-Shell Internal Ionization Accompanying β Decay. Y. Isozumi, T. Mukoyama and S. Shimizu. *Phys. Rev. Letters*, 29, 298 (1972).—Using an improved one-step theory of electron shakeoff, we have performed rigorous calculations of the energy-dependent K-shell internal ionization probability. The measured probability for ^{147}Pm considerably exceeds the theoretical curve at low electron energies. This suggests that

the direct collision process may play an important role when both a β particle and a K electron are emitted with low kinetic energies.

Effect of the Super-high Hydrostatic Pressure on the Nuclear Decay. H. Mazaki. *Butsuri*, **26**, 504 (1971), in Japanese.—A short sketch of the recent study on the effect of the super-high hydrostatic pressure on the decay constant of ^{99m}Tc , now in progress in Prof. Shimizu's Laboratory. The principle of the measurement and few details of the pressure machine being used are described. Some accounts on the future plan are also given.

K-Shell Internal Ionization Accompanying β Decay. Y. Isozumi and S. Shimizu. *Butsuri*, **27**, 44 (1972), in Japanese.—A short account on the historical development of the study is given. Some difficulties in the theories so far proposed and defects of the experiments so far performed are pointed out. Improved experimental techniques as well as the theoretical treatment endurable for reliable experimental results recently obtained by the authors are described.

A Pulse Shape Discriminator for an X-Ray Proportional Counter and its Application to a Coincidence Experiment. Y. Isozumi and S. Isozumi. *Nucl. Instr. and Meth.*, **96**, 317 (1971).—A pulse shape discrimination system has been developed for an X-ray proportional counter to reduce the background caused by high energy radiations, by the use of a modified time-to-pulse-height converter. Test measurements with argon filled counters have shown that the system is at least 90% effective in reducing the background in the energy range 6–15 keV, while more than 95% of all the X-ray signals can be accepted. Even in the 20–35 keV region, reasonably good results for the background reduction and the X-ray acceptance have also been obtained. The technique has been successfully applied to the coincidence experiment with two proportional counters in order to eliminate false coincidences due to unfavourable high energy radiations passing through both counters.

Analytical Chemistry

Some New Oxygenated Cobalt Complexes. M. Munakata. *Bull. Chem. Soc. Japan*, **44**, 1791 (1971).—Cobalt (II) complexes with ornithine, 2,4-diaminobutyric acid and 2,3-diaminopropionic acid were studied as new oxygen complexes. The former complex was reversibly, while the latter two complexes were irreversibly oxygenated at room temperature. These oxygenated complexes were diamagnetic and showed electronic absorption spectra similar to that of oxygenated cobalt histidine complex, and they were assumed to be O_2 -bridged binuclear complexes, $\text{L}_2\text{Co}-\text{O}_2-\text{CoL}_2$ (L: ligand). Cobalt and O_2 of the binuclear complexes existed in the state of Co(III) and O_2^{2-} , respectively. Thermodynamic measurements showed that oxygenation was an exothermal process, and deoxygenation an endothermal one. The reversibility correlated with the reduction potential of the central cobalt(III) ion and the enthalpy change of the oxygenation. Easier deoxygenation corresponded to more positive reduction potential and to smaller enthalpy change.

Gas Chromatography of Aluminum, Gallium, and Indium β -Diketone Chelates. K. Utsunomiya. *Bull. Chem. Soc. Japan*, **44**, 2688 (1971).—The gas-chromatographic behavior of aluminum(III), gallium(III), and indium(III) chelates with various β -diketones was investigated. The β -diketones studied were acetylacetone and 8 synthesized, alkyl-substituted acetylacetones, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone and its 5 synthesized alkyl derivatives, hexafluoroacetylacetone, benzoyltrifluoroacetone, furoyltrifluoroacetone, and thenoyltrifluoroacetone. The trifluoromethyl group increases the volatility of the chelates, while the aromatic group tends to decrease the volatility. In the alkyl-substituted acetylacetone series, the retention time of the chelates increases with an increase in the molecular weight, but it does not depend upon the volatility. On the other hand, the retention of the chelates containing the trifluoromethyl group is almost inversely correlated with the volatility.

Gas Chromatography of Rare Earth Pivaloyltrifluoroacetone Adducts with Tri-*n*-butyl Phosphate and Tri-*n*-octylphosphine Oxide. K. Utsunomiya and T. Shigematsu. *Bull. Chem. Soc. Japan*, **45**, 303 (1971).—The gas chromatography of the adduct compounds of europium (III), erbium (III), and lutetium (III) with pivaloyltrifluoroacetone (PTA) and tri-*n*-butyl phosphate (TBP), or with PTA and tri-*n*-octylphosphine oxide (TOPO) was studied.

The rare earth-PTA adducts with TBP or TOPO can gaschromatographed without decomposition. And reproducible linear relationships are obtained between the detector response and the concentration of aqueous rare earth ion solution in the HPTA-TBP-benzene extraction, and HPTA-TOPO—benzene extraction.

Thermogravimetric and Gas-chromatographic Study of Neodymium, Gadolinium and Erbium β -Diketone Chelates. K. Utsunomiya and T. Shigematsu. *Anal. Chim. Acta*, **58**, 411 (1972).—Various β -diketone chelates of neodymium, gadolinium and erbium were prepared. Hydrate formation and hydroxyl content of the chelates were studied by i.r. spectra in the region 3000–3700 cm^{-1} . The TGA curves of the chelates showed that dipivaloylmethane (DPM), isobutyrylpivaloylmethane (IBPM) and trifluoroacetylpivaloylmethane (TPM) chelates sublimed quantitatively at 150–270°; diisobutyrylmethane (Gd, Er), pivaloylpropionylmethane (Er), trifluoroacetylisobutyrylmethane (Gd, Er), trifluoroacetyl- α -methylbutyrylmethane (Er) and trifluoroacetylisovalerylmethane (Er) chelates partially volatilized, and the other chelates decomposed without sublimation. Generally, the anhydrous tris-chelates sublimed quantitatively, and the basic rare earth β -diketonates and hydrated chelates decomposed. Among the β -diketones studied HIBPM, HDPM and HTPM seem to be useful reagents for the gas chromatography of the rare earth elements.

Gas Chromatography of Rare Earth Chelates of Isobutyrylpivaloylmethane. K. Utsunomiya. *Anal. Chim. Acta*, **59**, 147 (1972).—Scandium, yttrium and the rare-earth IBPM chelates were prepared and their thermogravimetric and gas chromatographic behaviors were investigated. The possibility of direct determinations by measuring the peak height was also surveyed, although complete separation and simultaneous determination have still not been achieved.

Spectrophotometric Determination of Palladium with Pontachrome Azure Blue B. K. Uesugi, T. Shigematsu and M. Tabushi. *Anal. Chim. Acta*, **60**, 79 (1972).—A new spectrophotometric method for the determination of palladium with pontachrome azure blue B (Color Index 43830) as reagent is described. The palladium complex has maximal absorbance at pH 5.2–5.7 and at 605 nm. Beer's law is obeyed up to at least 2.5 p.p.m. of palladium; the molar absorptivity is $4.79 \cdot 10^4$ l mole⁻¹ cm⁻¹ and the sensitivity is $2.2 \cdot 10^{-3}$ μ g Pd cm⁻². The mole ratio of palladium and reagent in the complex is estimated to be 1:2. The formation constant of the complex is $5.0 \cdot 10^{10}$ under these conditions. Only copper (II) and iron (III) interfere with the determination of palladium when sodium fluoride is used as a masking agent.

Fluorometric Determination of Tin in Light Alloys with Rhodamine B. Y. Nishikawa, K. Hiraki, T. Naganuma and T. Shigematsu. *Japan Analyst*, **21**, 390 (1972), in Japanese.—A method for determining 0.002–0.1% of tin in light alloys (Al-base and Mg-base alloy) was investigated, and the following procedure was established. One gram of sample was dissolved with 40 ml of 4*N* hydrobromic acid and 1–2 drops of 30% H₂O₂. The solution was filtrated through a filter paper (No. 5A). The filter paper was then washed thoroughly with 4*N* hydrobromic acid, and the solution was diluted with 4*N* hydrobromic acid to 100.0 ml. A 0.5–10 ml portion of the solution was transferred to a 50 ml separating funnel, and tin was extracted into ethylether from the 4*N* HBr medium. The ether layer was transferred into 100 ml beaker, and evaporated gently. The residue was dissolved with 2*N* hydrobromic acid and transferred into a separating funnel. To the solution, 1.5 ml of 0.5% Rhodamine B solution and 5 ml of benzene were added, and the whole was shaken for 1 minute. The fluorescence intensity of the benzene solution was then measured. These procedures took 45 minutes, and 0.002–0.1% of tin in light alloys (Al-base and Mg-base alloy) could be determined.

Physical Chemistry

Molecular Vibrational Spectra of Tetracyanoquinodimethane and Tetracyanoquinodimethane-*d*₄ Crystals. T. Takenaka. *Spectrochim. Acta*, **27A**, 1735 (1971).—The infrared spectra of the TCNQ and TCNQ-*d*₄ crystals were observed with polarized radiations incident perpendicularly and obliquely upon the sample plane. From the results obtained, the observed bands were experimentally classified into the three infrared-active symmetry species on the assumption of the oriented gas model. The far-infrared spectra and the laser Raman spectra were also obtained for the TCNQ and TCNQ-*d*₄ samples. An assignment of the observed frequencies to the fundamental modes was made with the aid of the selection rule, the product rule, and the normal coordinate analysis of the in-plane vibrations carried out by using the basic and modified Urey-Bradley force fields. Some of the remaining frequencies were attributed to the overtone or combination vibrations with a good agreement between the calculated and observed values.

Studies of Built-up Films by Means of the Polarized Infrared ATR Spectrum. III. Elaidic Acid Films. T. Takenaka and K. Nogami. *Bull. Chem.*

Soc. Japan, **45**, 2367 (1972).—Attenuated total reflection studies with polarized infrared radiation have been made of multilayers of elaidic acid built up on a germanium plate by the Blodgett technique. It is concluded that the built-up films prepared from the tap-water substrate are made of calcium elaidate monohydrate. From the intensity changes in the regularly-spaced peaks (progression bands) in the region from 1350 to 1180 cm^{-1} , the planarity of the chain segment between the carboxylate group and the double bond is found to be dependent upon the surface pressure applied in the process of monolayer transfer onto the germanium plate. Studies of the anisotropy of the absorption index in the films show that the molecules assume a uniaxial orientation with respect to the axis normal to the germanium-sample interface (the z -axis), with an angle from 30° to 33° (in average) between the z -axis and the molecular axes. Furthermore, from the changes in the reflectivity with the number of layers, the film thickness per layer is estimated to be *ca.* 21.9 Å, a value which is in good agreement with the half-value of the long spacing, 44.16 Å, of the films as determined by X-ray diffraction studies. This apparently indicates that the films appear as the Y type.

X-Ray Crystal Structure of a 4:1 Amine Complex between Phthalocyanineiron (II) and 4-Methylpyridine. T. Kobayashi, F. Kurokawa, T. Ashida, N. Uyeda and E. Suito. *Chem. Commun.*, 1631 (1971).—A single-crystal X-ray diffraction study of the molecular complex between Fe^{II} phthalocyanine and 4-methylpyridine $[\text{C}_{32}\text{N}_8\text{H}_{16}\text{Fe}(\text{C}_6\text{NH}_7)_4]$ shows that two 4-methylpyridine molecules are coordinated at an octahedral Fe^{II} site with an N-Fe bond distance of 2.00 Å and that the other two are free molecules occluded in the structure.

Planar Defects of Cu_3Se_2 Crystals Produced by Solid-State Reaction. H. Morikawa. *Japanese J. of Appl. Phys.*, **11**, 431 (1972).—Electron microscopic observation has been carried out on some fine structures in the Cu_3Se_2 crystals which are formed by the reaction of vacuum-deposited selenium films with copper sheets. Two sorts of defects on the $[111]$ and $[021]$ planes were observed. These defects are ascribed to thin plate-shaped precipitation which may be a non-stoichiometric compound having a composition near to Cu_3Se_2 . A weak diffraction spot appearing near the $(\bar{1}/3, \bar{1}/3, 2/3)$ point is known to be due to the defects on the (021) plane.

Interstratified Layer Structure of the Organo-Montmorillonites as Revealed by Electron Microscopy. T. Yoshida and E. Suito. *J. Appl. Crystallography*, **5**, 119 (1972).—Layer structures of octadecylammonium-montmorillonite and trimethyloctadecylammonium: steramide-montmorillonite were studied by electron microscopy. Curled shapes of some lamella flakes of the organo-montmorillonites were found. Lattice images of the layers observed at the curled edges of the flake showed regular and irregular layer expansions caused by the interlayer adsorption of the organic compounds. Some of the results exhibited local variation of the layer expansion even within one particular layer. The local variation probably originated from the intrinsic nature of the montmorillonite layer. The arrangements of the alkyl chains of the adsorbed organic compounds between the layers of montmorillonite

were interpreted on the basis of interlayer distances obtained from the lattice images of the layers.

Extrusion Behavior of Hard Shale. M. Arakawa, S. Banerjee and W. O. Williamson. *The American Ceramic Society Bulletin*, **50**, 933 (1971).—A ground shale containing cemented mineral-aggregates and fine micaceous flakes, mixed with flocculating or dispersing aqueous solutions and ram-extruded, obeyed the expression $P = Ae^{-\alpha(\phi - \phi_0)}$, where P was the pressure which initiated extrusion, ϕ was the volume fraction of liquid, and A and α were constants. For five different mean particle-diameters, plots of $\log P$ against ϕ converged on common points, coordinates $\log P_0$ and ϕ_0 , irrespective of the flocculation or dispersion of the system. Pressures P_0 , unobtainable in the equipment, would probably fracture particles during extrusion because the limiting volume fraction ϕ_0 was relatively small. The slopes $-\alpha$ were less for flocculated than for dispersed particles, and they were less for smaller mean particle diameters in both flocculated and dispersed systems.

Percolation of Fine Powder through Packed Bed in Vibrating State. M. Arakawa and M. Nishino. *J. of the Society of Materials Science Japan*, **21**, 562 (1972), in Japanese.—The percolation of fine particles through packed bed of coarse powder was studied in the vibrating state. CaCO_3 , $\alpha\text{-Al}_2\text{O}_3$, glass beads, nylon powder, graphite and potato starch were used as sample powders. The percolation curves seemed to consist of two parts. In the initial state, the percolation weight increased rapidly. This is considered to show the process where fine particles tend to drain through every hole of the packing structure of coarse particles without mutual interactions between them. Then, in this region, the percolation rate increased as the particle size ratio of fine powder to coarse powder decreased. However, the percolation behaviors are dependent upon the kinds of materials and the properties of particle surface.

In the latter region where the increasing rate of percolation weight is very slow, it is considered that the movement of the fine particles through the packed bed is affected by the adhesion of fine particles to the surfaces of coarse powders. With combination of fine and coarse powders, the percolation curves are measured in various amplitudes of vibration. There are critical points at which the percolation weight in the initial region decrease rapidly with the decreasing amplitude. It is considered that the kinetic energy of fine particles at this critical point corresponds to the adhesive force between the fine particles and the coarse particles. This technique is considered to be available for the measurement of interaction force between the particles of different materials.

Direct Observation of Atoms and Molecules —Resolution of Electron Microscopy— N. Uyeda and E. Suito. *Nippon Kessho Gakkaishi*, **13**, 212 (1971), in Japanese. (Review).—The molecular image of organic compound with a moderate size was directly observed for the first time by high resolution electron microscopy. The formation of molecular images and the contrast inversion in the crystalline film of chlorinated Cu-phthalocyanine were interpreted in terms of the phase contrast

principle. The structure of thin crystal was determined on the basis of the molecular images observed and the electron diffraction pattern as well.

The World observed through Electron Microscope—The Structure of Organic Crystals— E. Suito, T. Kobayashi and N. Uyeda. *Kagaku no Ryoiki*, **26**, 66 (1972), in Japanese (Review).—The features of epitaxial films of organic crystals were revealed by electron microscopy and diffraction with respect to various compounds such as Pt- and Cu-phthalocyanines, chlorinated Cu-phthalocyanine, TCNQ, isoviolanthrone, indanthrone, violanthrone, flavanthrone, and perylene. The mechanism of crystal growth of these crystals is also explained.

How to See a Molecule through a Telescope. N. Uyeda. *Kagaku (Chemistry)*, **27**, 724 (1972), in Japanese (Review).—The principle of the optical diffraction is explained. Its application to X-ray and electron diffraction analyses and high resolution electron microscopy are also discussed in connection to the structure determination of organic molecules.

Dielectric Properties of Disperse Systems. T. Hanai. *Hyomen*, **6**, 326, 405, 524, 601, 668, (1968), **7**, 194, 383, 509, 646, 786, (1969), in Japanese.—This review article consisting of ten consecutive lectures gives an outline of current problems in the study of dielectric properties of disperse systems. In the introductory sections a little space is assigned for the explanation of some fundamental concepts on dielectric phenomena and for the principles of measuring dielectric constant and conductivity. A theory of interfacial polarization is described in detail in close connection with the dielectric characteristics observed for a variety of emulsions. Some disperse systems such as suspensions, gelatin gels, hydrosols and solubilized systems, show dielectric behavior different from the interfacial polarization, but the theoretical interpretation must await further study. Finally the differences of dielectric properties are shown between molecular solutions and heterogeneous systems.

The contents are as follows: 1. Introduction 2. Fundamental properties of dielectric phenomena 3. Experimental methods for studying dielectric properties 4. Theories of dielectric constants and of conductivities of heterogeneous systems 5. Theories of complex dielectric constants of heterogeneous disperse systems; Interfacial polarization due to heterogeneous structure 6. Experimental results for dielectric constants and the conductivities of emulsions; Confirmation of the interfacial polarization 7. Elementary explanation of dielectric dispersion due to the interfacial polarization 8. Some other types of frequency dependence of dielectric constants 9. Dielectric properties of some disperse systems 10. Dielectric theories of homogeneous systems; Molecular solutions 11. Comparison of the dielectric constants for various disperse conditions 12. Dielectric properties in relation to the flow states 13. Concluding remarks.

Dielectric Properties of the Mixtures of α -Fe₂O₃, TiO₂ and Fe₂TiO₅. K. Iwauchi, S. Yamamoto, Y. Bando, T. Hanai, N. Koizumi, T. Takada and S. Fukushima. *Japan. J. Appl. Phys.*, **10**, 1513 (1971).—Dielectric properties of various types of mixtures of α -Fe₂O₃, TiO₂, and Fe₂TiO₅ are investigated. Mixtures of α -Fe₂O₃ and Fe₂TiO₅,

and of TiO_2 and Fe_2TiO_5 powders respectively show the interfacial polarization. For these types of mixtures there are fairly good agreements between observed values of dielectric constant and calculated ones based on the Maxwell two layers model. On the other hand in the cases of the samples obtained by heating the mixture of $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 at 800°C observed values of dielectric constant are much larger than the calculated ones afforded by the Maxwell model. It seemed that dielectric constant in the interfacial polarization depends not only on the fraction of heterogeneous layers in the Maxwell model but also on their structures in the oxides. The Maxwell-Wagner interfacial polarization due to conductive oxides surrounding the surfaces of particles was found.

Dielectric Properties of Fine Particles of Fe_3O_4 and Some Ferrites.

K. Iwauchi. *Japan. J. Appl. Phys.*, **10**, 1520 (1971).—A study is made on the dispersions of resistivity and dielectric constant of $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , Zn ferrite, Mn ferrite, and MnZn ferrite fine particles over the frequency range of 10Hz to 1 MHz in the temperature range from 77°K to 300°K . The Maxwell-Wagner interfacial polarization arising from the heterogeneity of oxidation is observed in the fine particles of the oxides, except $\alpha\text{-Fe}_2\text{O}_3$, which are prepared from aqueous solutions of divalent metal salts as well as in the powders of ferrites containing ferrous ions which are prepared by the calcination at high temperatures. The structures of heterogeneity in the fine particles are explained by the model that there are high resistivity shells with poor ferrous ions on the surfaces of the particles.

Inorganic Chemistry

Inorganic Photochromic Materials: Compounds and Glasses. S. Sakka. *Zairyo-Kagaku (Materials Science)*, **8**, 101 (1971), in Japanese.—Photochromic properties of various crystals and glasses have been reviewed. Halide-activated photochromic glasses are characterized by ease of production and high reliability in coloring and fading properties (no fatigue).

Relation between Apparent Glass Transition Temperature and Liquidus Temperature for Inorganic Glasses. S. Sakka and J. D. Mackenzie. *J. Non-Crystalline Solids*, **6**, 145 (1971).—The ratio of the glass transition temperature T_g to the liquidus temperature T_l (or T_m) was calculated for a wide variety of inorganic glass forming systems including the elements, oxides and sulfides and technologically important systems such as borates and silicates. It was found that a simple empirical rule $T_g/T_l=2/3$ which was suggested for organic polymers holds surprisingly well for inorganic systems.

Observation of Glass Surfaces with Electron Microscope. T. Yamamoto. *Hyomen*, **10**, 174 (1971), in Japanese.—Review.

Ion Distribution of Manganese Ferrite Prepared by Wet Method. T. Takada, Y. Bando, M. Kiyama and T. Shinjo. *Proc. Int. Conf. Ferrite ed. by Y. Hoshino, Univ. of Tokyo Press*, 29 (1971).—The cation distribution of the manganese ferrite

$\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ prepared by wet method was investigated and it was found that about half of the manganese ions are present on B-sites, in contrast with the samples prepared by ceramic method. The lattice constants of samples prepared by wet method were smaller than those of the samples prepared by ceramic method and the difference of cation distribution accounts for this fact.

Preparation of Ferrites by Wet Method. T. Takada and M. Kiyama. *Proc. Int. Conf. Ferrites ed. by Y. Hoshino, Univ. of Tokyo Press*, 69 (1971).—Formation of spinel ferrites and barium ferrites by wet method was studied. For the spinel ferrites, the formation method, process, mechanism and especially formation conditions were examined in detail. It was found that spinel ferrite particles having a particle size between 0.05 and 1.0 μ could be prepared by oxidizing the aqueous solution containing ferrous and other divalent metal ions with air at temperatures below 100°C and used as a raw material for sintered ferrites. Moreover, a spinel ferrite whose chemical composition was $\text{M}_{1-x}\text{Fe}_{2+x}\text{O}_4$ could be prepared by this method. Formation of the compounds in the system $\text{BaO-Fe}_2\text{O}_3$ was studied using hydrothermal treatment. In this experiment, $\text{BaO-6Fe}_2\text{O}_3$, $\text{BaO-4.5Fe}_2\text{O}_3$ and $\text{BaO-2Fe}_2\text{O}_3$ precipitated depending on reaction conditions. Some properties of these ferrites were examined.

A New Preparation Method of the Oriented Ferrite Magnets. T. Takada, Y. Ikeda, H. Yoshinaga and Y. Bando. *Proc. Int. Conf. Ferrites ed. by Y. Hoshino, Univ. of Tokyo Press*, 275 (1971).—Oriented magnets were prepared by solid state reaction of oriented $\alpha\text{-FeOOH}$ or $\alpha\text{-Fe}_2\text{O}_3$ particles with nonoriented particles of BaCO_3 or SrCO_3 . Preparation of the oriented ferrite magnets was explained by a topotactic reaction between $\alpha\text{-Fe}_2\text{O}_3$ and carbonates. Topotactic change from $\alpha\text{-FeOOH}$ to $\text{SrO-6Fe}_2\text{O}_3$ was investigated by electron microscopy, and the crystallographic relationships among $\alpha\text{-FeOOH}$, $\alpha\text{-Fe}_2\text{O}_3$ and $\text{SrO-6Fe}_2\text{O}_3$ were determined as follows:

$$\begin{aligned} (100)_{\alpha\text{-FeOOH}} // (0001)_{\alpha\text{-Fe}_2\text{O}_3} // (0001)_{\text{SrO-6Fe}_2\text{O}_3} \\ [010]_{\alpha\text{-FeOOH}} // [11\bar{2}0]_{\alpha\text{-Fe}_2\text{O}_3} // [10\bar{1}0]_{\text{SrO-6Fe}_2\text{O}_3} \end{aligned}$$

The oriented $\alpha\text{-FeOOH}$ or $\alpha\text{-Fe}_2\text{O}_3$ compacts were obtained by uniaxial pressing. Particles of $\alpha\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$ in the compacts had the orientation of [100] axes and [0001] axes parallel to the direction of pressing, respectively. The magnetic properties of strontium and barium ferrite magnets obtained were measured.

Metal Insulator Phase Transition in $\text{V}_n\text{O}_{2n-1}$. S. Kachi, T. Takada, Y. Bando, K. Kosuge, H. Okinaka and K. Nagasawa. *Proc. Int. Conf. Ferrites ed. by Y. Hoshino, Univ. of Tokyo Press*, 563 (1971).—Research on the phase relation in the $\text{V}_2\text{O}_3\text{-V}_2\text{O}_4$ system confirmed that the following nine phases exist below 1400 K: V_2O_3 , V_3O_5 , V_4O_7 , V_5O_9 , V_6O_{11} , V_7O_{13} , V_8O_{15} , V_9O_{17} and VO_2 (generally expressed by $\text{V}_n\text{O}_{2n-1}$). The equilibrium oxygen partial pressure *vs.* temperature relation in this system also confirmed the presence of this homologous series. Electron diffraction study suggested that these belong to the “Shear Structure”.

Magnetic (magnetic susceptibility, Mössbauer effect) and electric (electrical conductivity, thermoelectric power) properties were also examined with single crystals,

which were prepared by a chemical transport reaction. As a result, it was revealed that these phases show a transition from a high-temperature metallic phase to a low-temperature semiconductive phase.

Mössbauer Evidence Against the Existence of Magnetically "Dead" Layers. T. Shinjo, T. Matsuzawa, T. Takada, S. Nasu and Y. Murakami. *Physics Letters*, **36A**, 489 (1971).— ^{57}Fe Mössbauer spectrum was measured for ^{57}Co source deposited on the surface of cobalt metal by electrolytic means. The result showed that the d-spin polarization in the surface is not decreased and it was evidenced that the magnetically "dead" layers do not exist.

Further Mössbauer Studies of Vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. T. Shinjo and H. Forstat. *J. Phys. Soc. Japan*, **31**, 1399 (1971).—The temperature dependence of internal magnetic fields in $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ was observed by the Mössbauer effect. It was made clear that although the temperature dependences of the two sublattices are greatly different, both internal fields disappear at the same temperature, 9.0 K. Measurements were also made at 4.2 K in the presence of an external field up to 50 kOe, whose direction was perpendicular to the crystal ac plane where the two spin easy directions are included. The ferromagnetic spin flipping occurred only at the sublattice of Fe I.

Nuclear Magnetic Resonance of Cr^{53} in Ferromagnetic CrO_2 . H. Nishihara, T. Tsuda, A. Hirai and T. Shinjo. *J. Phys. Soc. Japan*, **32**, 85 (1971).—NMR of Cr^{53} has been investigated on multidomain-, oriented singledomain- and impurity-contained samples of ferromagnetic CrO_2 . The hyperfine field at 0 K is found to be -154 ± 1 kOe when the moment is parallel to the *c*-axis, and its anisotropy to be 20 ± 5 kOe. A strong subsidiary line, corresponding to the hyperfine field of -111 ± 1 kOe, has been observed which would be presumably associated with chromiums affected by imperfections of the crystal. Nuclear spin-lattice relaxation time T_1 is inversely proportional to the absolute temperature *T* with $T_1 T = 15 \pm 3$ sec K. NMR of Mn^{55} is also observed in association with Mn^{4+} mixed in CrO_2 with a hyperfine field of 322 ± 2 kOe.

Iron Compounds Formed by the Aerial Oxidation of Ferrous Salt Solutions. M. Kiyama and T. Takada. *Bull. Chem. Soc. Japan*, **45**, 1923 (1972).—Aqueous solutions of ferrous salts have been oxidized at temperatures below 80°C to form iron compounds. By blowing the air into a FeCl_2 or a FeSO_4 solution, α - FeOOH precipitates and the pH decreases. As oxidation progresses, the concentration of ferric chloride or ferric sulfate increases and β - FeOOH or a basic sulfate begins to be newly formed. In these solutions the kinds of iron compounds formed do not depend strongly on the temperature. By oxidation of a FeBr_2 solution or a mixture of FeCl_2 and excess NaI solution, α - FeOOH , β - FeOOH and α - Fe_2O_3 are formed, depending on the temperature.

Formation of Titanic Oxides of Anatase, Brookite and Rutile Types by Aerial Oxidation of Titanous Solutions. M. Kiyama, T. Akita, Y. Tsutsumi

and T. Takada. *Chem. Letters*, 21 (1972).—Aerial oxidation of titanous solutions has been carried out at temperatures between 60° and 95°C. A desired one of titanic oxides of anatase, brookite and rutile types, can be obtained from strongly acidic solutions by selection of the kind and concentration of anions present and temperature.

Crystallography of V_nO_{2n-1} ($3 \leq n \leq 8$). K. Nagasawa, Y. Bando and T. Takada. *Mat. Res. Bull.*, 6, 833 (1971).—Single crystals of vanadium oxides, V_nO_{2n-1} ($3 \leq n \leq 8$), which were synthesized by the chemical transport method, have been studied by the X-ray single crystal method. The lattice (a_n , b_n and c_n) of the homologous series with $4 \leq n \leq 8$ can be systematically described on the basis of the parent rutile-type lattice (a_r , b_r and c_r) as follows: $a_n = -a_r + c_r$, $b_n = a_r + b_r + c_r$ and $c_n = 1/2(2n-1)(b_r + c_r)$. These relations can be explained on the basis of the 'shear' structures of V_nO_{2n-1} described by Andersson and Jahnberg (1963). The crystal of V_3O_4 has been found to belong to the space group $P2_1/n$, but can be related to the homologous series of V_nO_{2n-1} by adopting the lattice with $2a_n$, b_n and c_n .

Crystal Growth of V_nO_{2n-1} ($3 \leq n \leq 8$) by the Chemical Transport Reaction and Electrical Properties. K. Nagasawa. *Mat. Res. Bull.*, 6, 853 (1971).—Single crystals of the intermediate vanadium oxides between V_2O_3 and VO_2 with the general formula V_nO_{2n-1} ($3 \leq n \leq 8$) were grown by the chemical transport reaction using $TeCl_4$ as a transport agent. The reactions were carried out in sealed tubes with the temperature gradient between 1050°C and 950°C. The sizes of crystals produced were about 1~10 mm. The electrical properties of the crystals are summarized.

Dielectric Properties of the Mixtures of α - Fe_2O_3 , TiO_2 and Fe_2TiO_5 . K. Iwauchi, S. Yamamoto, Y. Bando, T. Hanai, N. Koizumi, T. Takada and S. Fukushima. *J. J. Appl. Phys.*, 10, 1513 (1971).—Dielectric properties of various types of mixtures of α - Fe_2O_3 , TiO_2 , and Fe_2TiO_5 are investigated. Mixtures of α - Fe_2O_3 and Fe_2TiO_5 and of TiO_2 powders respectively show the interfacial polarization. For these types of mixtures there are fairly good agreements between observed values of dielectric constant and calculated ones based on the Maxwell two layers model. On the other hand in the cases of the samples obtained by heating the mixture of α - Fe_2O_3 and TiO_2 at 800°C observed values of dielectric constant are much larger than the calculated ones afforded by the Maxwell model. It seemed that dielectric constant in the interfacial polarization depends not only on the fraction of heterogeneous layers in the Maxwell model but also on their structures in the oxides. The Maxwell-Wagner interfacial polarization due to conductive oxides surrounding the surfaces of particles was found.

Organic Chemistry

Eupacunin, a Novel Antileukemic Sesquiterpene Lactone from *Eupatorium cuneifolium*. S. Morris Kupchan, M. Maruyama, R. J. Hemingway, J. C. Hemingway, S. Shibuya, T. Fujita, P. D. Cradwick, A. D. U. Hardy and

G. A. Sim. *J. Amer. Chem. Soc.*, **93**, 4914 (1971).—The isolation and structural elucidation of eupacunin, a novel germacranolide from *E. cuneifolium* (Town) L., are reported. Eupacunin has significant antileukemic and tumor inhibitory properties, and appears to be the first recognized germacranolide *cis, cis*-diene. The structure was postulated from degradative and spectral studies of eupacunin and its companion cytotoxic lactones eupacunoxin, and eupatocunin. Unequivocal proof of structure and configuration was achieved by X-ray crystallographic analyses of eupacunin *o*-bromobenzoate and eupacunoxin *m*-bromobenzoate.

Liatrin, a Novel Antileukemic Sesquiterpene Lactone from *Liatris chapmanii*. S. Morris Kupchan, Vivian H. Davis, Tetsuro Fujita, Michael R. Cox and Robert F. Bryan. *J. Amer. Chem. Soc.*, **93**, 4916 (1971).—The isolation and structural elucidation of liatrin, a novel germacranolide from *L. chapmanii*, are reported. Liatrin has significant antileukemic activity in mice and appears to be the second recognized naturally occurring germacranolide *cis, cis*-diene. The structure was postulated from degradative and spectral studies of liatrin, and proven by X-ray crystallographic analysis of the *o*-bromobenzoate of the diol obtained by reduction of liatrin with sodium borohydride.

Absolute Configuration of Lythrancine-I, -II, -III, -IV, Lythrancepine-I, -II, and -III. E. Fujita and Y. Saeki. *Chem. Pharm. Bull.* (Tokyo), **19**, 1515 (1971).—Seven new alkaloids shown in the title were isolated from *Lythrum anceps* Makino, and their structures were already elucidated by us. Here, their absolute configuration is discussed.

First of all, the NMR spectrum (100 MHz) of lythrancine-IV was investigated in detail, and the relative stereochemistry was almost clarified. Subsequently, lythrancepine-II was converted into a lythranine-type derivative, which was proved to be the antipode of a compound derived from lythranidine having the known absolute configuration. The other spectroscopic data, for instance the ORD spectrum of dehydrolythrancine-III, supported the result of the chemical conversion. Thus, the absolute configuration of the seven bases was established unequivocally.

Lythraceous Alkaloids. V. Isolation of Ten Alkaloids from *Lythrum anceps*. E. Fujita, K. Bessho, Y. Saeki, M. Ochiai and K. Fuji. *Lloydia*, **34**, 306 (1971).—Isolation of ten new alkaloids, lythranine, lythranidine, lythramine, lythrancine-I, -II, -III, -IV, lythrancepine-I, -II, and -III, from *Lythrum anceps* Makino is described.

Terpenoids-XIX. Chemical Conversion of Enmein into *ent*-15-Kaurene and *ent*-16-Kaurene. E. Fujita, T. Fujita and Y. Nagao. *Tetrahedron*, **28**, 555 (1972).—Enmein, the major bitter diterpenoid of *Isodon trichocarpus* Kudo and *I. japonicus* Hara, was converted into *ent*-15-kaurene, *ent*-16-kaurene, and *ent*-kaurane via many steps of reactions. The new findings obtained during the synthesis and some interesting mechanisms were discussed.

Studies on the Alkaloids of *Thalictrum Thunbergii* DC. XVIII. Total Synthesis of Optically Active Natural O-Methylthalicberine. E. Fujita, A. Sumi, and Y. Yoshimura. *Chem. Pharm. Bull. (Tokyo)*, **20**, 368 (1972).—Optically active O-methylthalicberine, a major bisbenzylisoquinoline-type alkaloid of *Thalictrum Thunbergii* DC., was synthesized through a number of steps of reactions. A preliminary confirmation of its structure was also described.

Terpenoids. Part XVIII. A Common Stereoelectronic Requirement in Epimerisations and Retro-Dieckmann-type Cleavages of Some Diterpene Alcohols and Ketones. E. Fujita and Y. Nagao. *J. Chem. Soc. (C)*, 2902 (1971).—The mechanism of the epimerisation of the alcohols derived from enmein was discussed in the light of the stereoelectronic factor. These alcohols belong to the B-secokaurane derivative, and the epimerisation occurs by treatment of the alcohols which have a *cis*-relationship between the 15-hydroxy- and 16-methyl groups with weak alkali. The products are the corresponding *trans*-alcohols.

The investigation found a common stereoelectronic requirement in several analogous epimerisations in alcohols and ketones of B-secokaurane derivatives and gibberellins.

The Carboxylation Reaction Using Nickel Catalysts. V. The Catalytic Reaction of Propene with Nickel Carbonyl and Nickel Carbonyl-Triphenylphosphine. S. Kunichika, Y. Sakakibara, T. Okamoto and K. Takagi. *Bull. Chem. Soc. Japan*, **44**, 3405 (1971).—The carboxylation reaction of propene catalyzed by nickel carbonyl was studied under various conditions. Iso- and *n*-butyric acids were obtained in good yields under mild conditions in the presence of a large amount of an organic acid. The catalytic carboxylation area was examined in detail. The carboxylation reaction proceeded smoothly in tetrahydrofuran, acetic acid, and dioxane. The proportion of isobutyric acid was largest in acetic acid (72.5–77.5%). Triphenylphosphine (TPP) had a great effect on the reaction rate, the catalytic reaction area, and the product distribution. On the reaction mechanism, an active species (HNi (CO) (TPP)X) was taken to account for the experimental results.

Studies on the Reaction of Malonic Ester with Formaldehyde. S. Kunichika, S. Oka, T. Sugiyama, K. Nakamura and K. Fukui. *Nippon Kagaku Kaishi*, **1**, 596 (1972), in Japanese.—The reaction of diethyl malonate with formaldehyde in acetic acid in the presence of copper acetate gave a mixture of diethyl bishydroxymethylmalonate, diethyl acetoxymethylmalonate, and diethyl bisacetoxymethylmalonate contrary to the previous report that the product was diethyl hydroxymethylmalonate. Distillation of diethyl bishydroxymethylmalonate and diethyl acetoxymethylhydroxymethylmalonate in the presence of copper acetate afforded diethylmethylenemalonate in yields of 80%, and 70%, respectively. A reaction path has been proposed.

Friedel-Crafts Rearrangements of 1-Phenyl-2-tolyethanes. S. Kunichika, S. Oka, T. Sugiyama and M. Ichii. *Nippon Kagaku Zasshi*, **92**, 801 (1971), in Japanese.—The AlBr₃.HBr-induced rearrangement reactions of 1-phenyl-2-tolyethanes (PTE) have been studied in various solvents. In each case the samples were taken periodically

and analyzed by vapor phase chromatography. When the reaction started from any of *o*-, *m*-, and *p*-PTE isomers at 50°C in benzene, initially the PTE isomer mixture attained a constant distribution (5% *O*-, 78% *m*-, and 17% *p*-), and then 1,2-diphenylethane (DPE) produced by the accompanying transalkylation of the 2-phenylethyl group to benzene increased gradually. In initial stages of the reactions, DPE was formed faster from *o*- and *p*-isomers than from *m*-isomer. Under the same conditions, PTE in toluene were transalkylated to 1,2-ditolylethanes (DTE) as slowly as in benzene, showing the several constant distributions of the isomers of PTE and DTE. These results suggest that the isomerization in PTE proceeds rapidly by an intramolecular 1,2-shift and that the transalkylation by the arylalkyl cation-alkylation mechanism which involves the preferential hydride abstraction.

Reaction of Chloramines Part II. The Reaction of Chloramines with β -diketones. J. Oda, M. Horiike and Y. Inouye. *Agr. Biol. Chem.*, **35**, 1648 (1971).—Chloramine and *N*-dialkylchloramines readily reacted with 1,3-diketones even in the absence of base to afford the corresponding fragmentation products, amides and dichloroketones in better yields. The experimental results revealed that the reaction was initiated by the attack of Cl^+ , and another molecule of chloramine attacked the enolic $\text{C}=\text{C}$ double bond of the produced intermediary 3-chloroacetylacetone. Subsequently the C-C bond fission proceeded via a concerted cyclic mechanism. The cyclic concerted mechanism was cogently rationalized by the reaction with a cyclic 1,3-diketone, dimedone, in which the 6-membered cyclic chelation can not be accommodated in the transition state by virtue of the structure of the substrate, and gave rise to 2-chloro-dimedone alone.

Thermal Behavior of Allethrin at 150°C in Atmospheric Environment. N. Baba and M. Ohno. *Agr. Biol. Chem.*, **36**, 56 (1972).—Vaporization of allethrin was investigated by heating as such at 150°C in the atmosphere. Total vaporization rate, purity of allethrin in vapor and that of the remaining residue were determined for α -DL-*trans*-allethrin, *cis*-allethrin and the mixture of isomers of allethrin by means of glc method. Structural elucidation of the pyrolysis products in vapor revealed the presence of free *trans*-chrysanthemic acid, allethrolone and 2-allyl-3-methylcyclopent-2-ene-1,4-dione in the vapor from α -DL-*trans*-allethrin. In addition to these compounds, *cis*-dihydrochrysanthemo- δ -lactone and pyrocin were found in the vapor from the mixture of 8 isomers of allethrin, while the vapor phase of heated *cis*-allethrin contained *cis*-dihydrochrysanthemo- δ -lactone along with the 3 main compounds.

The Reaction of Enamines with *N*-dialkylchloramines. T. Wada, J. Oda and Y. Inouye. *Agr. Biol. Chem.*, **36**, 799 (1972).—The reaction of dialkylchloramines with *N*-dialkyl-substituted aminoisobutenes was shown to give a mixture of the two α -dialkylaminoaldehydes, which were derived not only from the addition of chloramine, but also from the rearrangement of amino group in the parent enamines. The results suggested an ionic path involving a cyclic dialkylaziridinium ion as intermediate. The possible mechanism of these reaction was discussed.

Solvent Effect in a Partial Asymmetric Synthesis. III. K. Nishiyama and Y. Inouye. *Bull. Chem. Soc. Japan*, **44**, 2795 (1971).—The solvent polarity-dependence of asymmetric synthesis was unambiguously corroborated in the Michael type cyclopropane formation in a system designed so as to proceed through the transition state conformations of an equal dipole moment not involving any geometrical isomerism: the NaH-catalyzed condensation of (–)-methyl methacrylate with ethyl chloromalonate in solvent media of varying polarity resulted in the formation of (–)-1-methyl-cyclopropane-1,2,2-tricarboxylic acid having the same sign of rotation in all cases. The fit of the stereochemistry to the Kirkwood equation was borne out by the linearity found for the plots of $\log R/S$ against the Kirkwood-Onsager parameter. The R-configuration of (–)-1-methylcyclopropane-1,2,2-tricarboxylic acid was established by the correlation to (+)-2,2-diphenyl-1-methylcyclopropanecarboxylic acid of the well-defined R-configuration.

Syntheses and Reactions of Alkoxythallated Compounds. S. Uemura and K. Ichikawa. "Reactive Intermediates." (A), *Kagaku Dojin, Kyoto*, 159 (1971), in Japanese.—Review.

Organic Reactions by Thallium Salts. K. Ichikawa and S. Uemura. *Yūki Gōsei Kagaku Kyōkai-shi*, **29**, 400 (1971), in Japanese.—Review.

The Chlorination of Cyclooctadiene with Cupric Chloride in Acetonitrile Containing Lithium Chloride. S. Uemura, A. Tabata, Y. Kimura and K. Ichikawa. *Bull. Chem. Soc. Japan*, **44**, 1973 (1971).—The chlorination of 1,3- and 1,5-cyclooctadiene with copper (II) chloride in acetonitrile containing LiCl at 80° for 22 hr afforded 3,4-dichloro- and 5,6-dichlorocyclooctene (*trans* and *cis* mixtures) respectively. The results with acrylonitrile and *trans*-crotyl chloride as reference substrates are also reported, and all results are compared with those obtained by conventional chlorine gas chlorinations.

Aromatic Bromination by the Use of Organic and Inorganic Thallium Salts. S. Uemura, K. Sohma, M. Okano, and K. Ichikawa. *Bull. Chem. Soc. Japan*, **44**, 2490 (1971).—Using organic and inorganic Tl salts, the following aromatic brominations were carried out in a CCl₄ or HOAc solvent and were found to occur very smoothly; (A) aromatic bromination with TlBr₃·4H₂O, (B) aromatic bromination with Br₂ in the presence of Tl (III) and Tl(I) salts, and (C) the bromination of arylthallium (III) compounds. From a study of the relative rates and selectivities of benzene and toluene, it was deduced that an arylthallium (III) compound was not involved as an intermediate in the A and B reactions, that Tl (III) salts were more effective catalysts than Tl (I) salts for the B bromination, and that the A reaction was essentially identical with the B reaction with the TlBr₃·4H₂O catalyst. By considering the difference in the catalytic behavior of Tl (III) and Tl (I) salts in the B reaction, probable mechanisms are suggested.

Explosion during the Preparation of Ethylphenyl Thallic Acetate Perchlorate. S. Uemura, Y. Ikeda, O. Itoh and K. Ichikawa. *Bull. Chem. Soc. Japan*,

44, 2571 (1971).—During the preparation of ethylphenyl thallic acetate perchlorate using $\text{TI}(\text{OAc})_3$, HClO_4 , ethylbenzene and acetic acid, the violent explosion occurred in the last stage of concentration of the reaction mixture. Care should be taken during the process of evaporating the solvent and too much evaporation should be avoided. Reactions in DMSO with HClO_4 should also be avoided.

Thallium (III) Chloride Tetrahydrate as a Lewis Acid Catalyst for Aromatic Alkylation and Acylation. S. Uemura, K. Sohma and M. Okano. *Bull. Chem. Soc. Japan*, **45**, 860 (1972).—From a study of aromatic alkylation and acylation using $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ catalyst, it was revealed that this metal chloride was a milder Lewis acid catalyst than AlCl_3 and FeCl_3 and was similar in activity to ZnCl_2 . Although the yields of the products were generally low, the characteristics of this catalyst were observed in the formation of β, β' -dimethylstyrene and benzoylacetone upon the respective methallylation and acetylation of benzene and in the fact that the hydrated chloride was more effective than the anhydrous one. In a sharp contrast to aromatic bromination, $\text{TI}(\text{OAc})_3$ showed little activity in these reactions.

Chlorination of Olefins with Thallium (III) Chloride Tetrahydrate. S. Uemura, O. Sasaki, and M. Okano. *Bull. Chem. Soc. Japan*, **45**, 1482 (1972).—In CCl_4 , $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ reacted with mono- and diolefins to give *vic*-dichlorinated compounds (I) in 20–41% yields together with monochlorinated ones (II). The yields of I were intensely increased by adding $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or FeCl_3 and bubbling oxygen into the reaction system, although such additives alone gave none of I in CCl_4 . In acetic acid, the reaction gave diacetoxylated compound. As to the *vic*-dichlorination, it was proposed that the reacting species was a polarized form of dimeric TiCl_3 and not free chlorine evolved from $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$.

Reaction of Arylthallium (III) Compounds with Copper (II) and (I) Cyanides. Synthesis of Aryl Cyanide. S. Uemura, Y. Ikeda and K. Ichikawa. *Tetrahedron*, **28**, 3025 (1972).—Various kinds of arylthallium (III) salts react with copper (II) or (I) cyanide in acetonitrile or pyridine to give the corresponding aryl cyanides in good yield. In acrylonitrile the reaction using copper (I) cyanide was revealed to be of an ionic concerted intermolecular and not radical type.

Reaction of Alkoxythallium (III) Compounds of Olefins with Palladium (II) Chloride. Evidence of TI-Pd Exchange in Oxymetallates. S. Uemura, K. Zushi and M. Okano. *Chem. Commun.*, 234 (1972).—Treatment of alkoxythallates of styrene with PdCl_2 in MeOH gave acetophenone or its alkyl acetal through TI-Pd transmetallation.

Sodium Borohydride Reduction of Alkoxythallated Compounds of Olefins. S. Uemura, A. Tabata and M. Okano. *Chem. Commun.*, 517 (1972).—Alkaline NaBH_4 reduction of alkoxythallated compounds of olefins gives a mixture of the parent olefins, alkyl ethers, and dialkylthallium compounds; hydrogen for replacement of thallium arises from the solvent and not from NaBH_4 .

Selective *cis*-Chlorination of Olefins by Antimony(v) Chloride. S. Uemura, O. Sasaki and M. Okano. *Chem. Commun.*, 1064 (1971).—Treatment of olefins with SbCl_5 in CCl_4 gave *cis-vic*-dichloroalkanes predominantly; e.g. *cis*- and *trans*-but-2-enes and cyclohexene gave *meso*- and (\pm)-2,3-dichlorobutanes and *cis*-1,2-dichlorocyclohexane respectively.

Polymer Chemistry

Recent Experimental Aspects of Non-Linear Viscoelasticity. M. Kurata. *J. Soc. Material Sci. Japan*, **21**, 360 (1972), in Japanese.—A review article of the recent experimental studies on the non-linear viscoelasticity of polymer solutions and melts. The subjects covered are:

(1) Non-Newtonian viscosity behavior of narrow-distribution polymers, (2) the normal stress effect in steady shear flow, (3) the recoverable strain in steady shear flow, (4) the stress relaxation after the cessation or interruption of steady shear flow, (5) the growth of stress after the onset of the steady shear flow, (6) the recoverable strain during the approach to the steady shear flow, (7) the sinusoidal oscillation superimposed on the steady shear flow, and (8) the stress relaxation under larger shear strain. It is specially noted that the distribution function of relaxation time obtained with a constant rate of deformation is appreciably shifted to be made on short time scale, depending on the deformation rate, while the distribution function obtained with a constant deformation is not. Emphasis is also put on the key rôle of the recoverable strain measurements in the study of non-linear viscoelasticity.

The Concentration Dependence of Steady-State Compliance for Polymer Solutions. Y. Einaga, M. Kurata, T. Sugie and M. Tamura. *J. Soc. Material Sci. Japan*, **21**, 453 (1972), in Japanese.—The steady-state compliance J_e as a function of the molecular weight M and the concentration c for polymer solution can be expressed as:

$$\begin{aligned} J_e &= \alpha M / cRT && \text{for smaller values of } c \text{ or } M \\ &= \beta M^0 / c^{2-3} && \text{for larger values of } c \text{ and } M \end{aligned}$$

Here α and β are constants and RT is used in its usual meaning. The second behavior of J_e is characteristic of highly entangled system. In the concentration range where the transition from the first to the second behavior occurs, the J_e displays the maximum.

Either of the two relaxation spectra, A and B , are found to be compatible with these observed behaviors of J_e . These are:

$$\begin{aligned} \text{(A)} \quad H_W(\tau) &= \frac{1}{2} \frac{cRT}{M_e} \left(\frac{\tau_c}{\tau} \right)^{1/2} && 0 < \tau < \tau_c \\ H_I(\tau) &= \frac{1}{2} (1 - g_N) \frac{cRT}{M_e} \left(\frac{\tau_c}{\tau} \right)^{1/2} && \tau_c < \tau < \tau_l \\ H_B(\tau) &= \frac{1}{h} g_N \frac{cRT}{M_e} && \tau_l < \tau < \tau_m \\ \tau_c &= \tau_l E^{-2}, \quad \tau_m = \tau_c E^{3.5}, \quad \tau_l = \tau_m e^{h(1/E-1)} \end{aligned}$$

$$\begin{aligned}
\text{(B)} \quad H_W(\tau) &= \frac{1.75}{3} \frac{cRT}{M_e} \left(\frac{\tau_c}{\tau} \right)^{2/3} & 0 < \tau < \tau_c \\
H_Z(\tau) &= \frac{1.75}{3} (1 - g_N) \frac{cRT}{M_e} \left(\frac{\tau_c}{\tau} \right)^{2/3} & \tau_c < \tau < \tau_l \\
H_B(\tau) &= \frac{1}{h} g_N \frac{cRT}{M_e} & \tau_l < \tau < \tau_m \\
\tau_c &= \tau_1 E^{-1.5}, \quad \tau_m = \tau_c E^{3.5}, \quad \tau_l = \tau_m e^{1.75h(1/E-1)/2}
\end{aligned}$$

The former corresponds to the Rouse theory, while the latter to the Zimm theory. Here, τ_1 represents the maximum relaxation time of the original Rouse or Zimm theory, M_e is entanglement spacing, E is the number of entanglement point in a molecule, hence $E = M/M_e$, and g_N and h are parameters representing the intensities of H_1 and H_B , respectively.

The viscosity η , storage modulus G' and loss modulus G'' are also calculated on the basis of these spectra. These results are qualitatively in agreement with the observed one, particularly in the case of high value of h and low value of g_N .

Characterization of Branched Polymers. M. Kurata *J. Soc. Rubber Ind., Japan*, **45**, 105 (1972), in Japanese.—Review article on the method of characterization of branched macromolecules. The subjects covered are: (1) Average molecular weights and their treatment, (2) Statistical aspects of random branching, (3) Dilute solution properties of randomly branched polymers, (4) Gel permeation chromatography of randomly branched polymers, (5) Computer analysis of the intrinsic viscosity and the GPC elution curve of randomly branched polymers.

Dynamic Mechanical Properties of Moderately Concentrated Polystyrene Solutions. L. A. Holmes, S. Kusamizu, K. Osaki and J. D. Ferry. *J. Polymer Sci., Part A-2*, **9**, 2009 (1971).—The storage (G') and loss (G'') shear moduli have been measured in the frequency range from 0.04 to 630 Hz for solutions of narrow distribution polystyrenes with molecular weights (M) 19,800 to 860,000, and a few of poly (vinyl acetate), $M=240,000$. The concentration (c) range was 0.014–0.40 g/ml and the viscosities of the solvents (diethyl phthalate and chlorinated diphenyls) ranged from 0.12 to 70 poise. Data at different temperatures (0–40°C) were combined by the method of reduced variables. Two types of behavior departing from the usual frequency dependence describable by the Rouse-Zimm-Tschoegl theories were observed. First, for $M \cong 20,000$, the ratio $(G'' - \omega\eta_s)/G'$ in the neighborhood of $\omega\tau_1 = 1$ was abnormally large and the steady-state compliance J_e^0 was abnormally small, especially at the lowest concentrations studied. Here ω is circular frequency, η_s solvent viscosity, and τ_1 terminal relaxation time. Related anomalies have been observed by others in undiluted polymers at still lower molecular weights. Second, at the highest concentrations and molecular weights, a “crossover” region of the logarithmic frequency scale appeared in which $G'' - \omega\eta_s < G'$. The width of this region is a linear function of $\log c$; the frequency dependence under these conditions can be represented by a sequence of Rouse relaxation times grafted on to a sequence of Zimm relaxation times. For each molecular weight, the terminal relaxation time τ_1 was

approximately a single function of c for different solvents of widely different viscosities of widely different η_s . At lower concentrations, τ_1 was close to the Rouse prediction of $6\eta M/\pi^2 cRT$, where η is the steady-flow viscosity; but at higher concentrations, τ_1 was proportional to η/c^2 and corresponded, according to a recent theory of Graessley, to an average molecular weight of 20,000 between entanglement coupling points in the undiluted polymer.

Infinite-Dilution Viscoelastic Properties of Linear and Star-Shaped Polybutadienes. K. Osaki, Y. Mitsuda, R. M. Johnson, J. L. Schrag and J. D. Ferry. *Macromolecules*, 5, 17 (1972).—The Birnboim-Schrag multiple-lumped resonator has been used to measure storage (G') and loss (G'') shear moduli, in the concentration range (c) from 0.0005 to 0.006 g/ml, of two linear and one four-armed star 1,4-polybutadiene, in three different good solvents. The frequency range was from 106 to 6050 Hz. Analysis of the concentration dependence of G'/c and $(G'' - \omega\eta_s)/c$, where ω is radian frequency and η_s is solvent viscosity, showed that the longest relaxation time is affected much more than others by incipient intermolecular interactions. The above quantities extrapolated to zero concentration, i.e., $[G']$ and $[G'']$, were compared with the Zimm and Zimm-Kilb theories. The data for the linear polymers (molecular weights 2.2 and 9.1×10^5) agreed closely with the Zimm theory, using exact eigenvalues, with the hydrodynamic interaction parameter $h = 0.15$ and the number of submolecules N large; the reduced frequency range was 2.8 decades. The data for the star polymer (molecular weight 5.0×10^5) agreed closely with the Zimm-Kilb theory, using exact eigenvalues, with $h = 0.10$ and N large; the reduced frequency range was 2.2 decades. The frequency dependence of viscoelastic properties for the star polymer showed several distinctive features.

A Revised Version of the Integrodifferential Equation in the Zimm Theory for Polymer Solution Dynamics. K. Osaki. *Macromolecules*, 5, 141 (1972).—Some of the viscoelastic quantities provided by the bead-spring model theory of Zimm have been reevaluated with the use of a new version of the integrodifferential equation, revising the numerical solutions of Tschoegl for intermediate degrees of hydrodynamic interaction. Comparison for low numbers of submolecules (N) with the result of the exact solution of Zimm's eigenvalue problem by Lodge and Wu reveals that the revised version (in contrast with the original) gives almost identical results for dynamic-mechanical properties and intrinsic viscosity. Numerical results showed that the quantities previously regarded as determined solely by the hydrodynamic interaction parameter h depend also on N even if N is not very small. An apparent non-free-draining" effect is expected for the intrinsic viscosity irrespective of the value of h if $h/N^{1/2}$ is close to 0.25.

Infinite-Dilution Viscoelastic Properties of Poly (α -methylstyrene). Applications of Zimm Theory with Exact Eigenvalues. K. Osaki, J. L. Schrag and J. D. Ferry. *Macromolecules*, 5, 144 (1972).—The storage and loss shear moduli have been measured for solutions of poly (α -methylstyrene) with narrow-distribution molecular weight of 1.43×10^6 in α -chloronaphthalene and decalin. The measurements

were performed with the Birnboim-Schrag multiple-lumped resonator at nine frequencies from 100 to 6000 Hz; the data at each frequency were extrapolated to zero concentration to obtain the intrinsic storage and loss moduli. The extrapolated results for poly (α -methylstyrene) as well as previously published results for polystyrene and polybutadiene solutions were compared with the exact numerical result of the bead-spring model theory of Zimm as evaluated by Lodge and Wu for finite numbers of beads and various values of the hydrodynamic interaction parameter h . The theory reproduced the experimental data with reasonable values of h except for a small deviation at high frequency in the case of poly (α -methylstyrene), which was apparently due to the effect describable by the internal viscosity of the Peterlin theory. Values of h obtained from the comparison increased from 0.1 to 0.25 as the solvent powder decreased and were not very sensitive to the choice of the polymer and solvent not to the molecular weight of the polymer. The product $a_\eta h$, where a_η is the expansion factor of the excluded volume effect as evaluated from the intrinsic viscosity, had an approximately constant value of 0.21 for most of the systems examined. This result suggested that the assumption of uniform expansion of effective segment length due to the excluded volume effect is sufficient to explain the effect of solvent power on the observed spectrum of viscoelastic relaxation times.

Rayleigh Scattering by Linear Flexible Macromolecules. H. Utiyama, Y. Tsunashima and M. Kurata. *J. Chem. Phys.*, **55**, 3133 (1971).—Precise light-scattering measurements were made on poly- α -methylstyrene samples with sharp molecular weight distribution, the molecular weight ranging from about 400 thousand to 7 million. The specific reduced scattered intensity at infinite dilution was determined for 18 scattering angles in the range of 9° – 150° , in trans-decalin at 9.6° (theta temperature), 15.2 , 29.4 , 91.3°C , and in benzene at 30.0°C . In trans-decalin, the particle scattering factor P obtained is in good agreement with the well-known Debye equation irrespective of the temperature and the molecular weight. Experimental results in good solvent, benzene, are also well represented by the Debye equation for $1 \geq P \geq 0.15$, but significant deviation is observed for $P < 0.15$. All the experimental data can be fitted to a theory in which the generalized Domb-Gillis-Wilmers distribution function for end-to-end distances R , $\Phi_N(R) = C_N R^l \exp[-(R/\sigma)^t]$, is used for polymer chains of N segments with excluded volume effects. C_N is the normalizing constant; σ is related to the standard deviation of R ; and $t = 2/(1-\epsilon)$, where ϵ is defined by $\langle R^2 \rangle = AN^{1+\epsilon}$. A is a numerical constant. The parameter l obtained by fitting the experimental data to the theory was found to increase with ϵ and to be slightly greater than t .

Measurements of Anisotropic Light Scattering and Thermal Transition in Optical Anisotropy of Poly- α -methylstyrene. H. Utiyama and Y. Tsunashima. *J. Chem. Phys.*, **56**, 1626 (1972).—The anisotropic optical scattering from solutions of flexible macromolecules is discussed, and a simple experimental method of obtaining information concerning the optical anisotropy of a segment is presented. Intensities of anisotropic and isotropic optical scattering have been measured on poly- α -methylstyrene samples in the ranges of molecular weight from 400 thousand to 7 million, in

trans-decalin at 9.6° (theta temperature), 20.2°, 29.5°, 49.7°, and 91.6°C. Analysis of the experimental data by the present method shows that the optical anisotropy of poly- α -methylstyrene exhibits a transitionlike decrease with temperature with the midpoint of about 30°C. The origin of the slight cooperativity of the transition is discussed and concluded as indicative of the correlation between the skeletal bond rotation and the rotational motion of the phenyl group. Some change of the unperturbed mean-square radius of gyration with temperature is suggested as a possible consequence of the transition.

Light Scattering Instruments. H. Utiyama. *Chapter 3 in a monograph, "Light Scattering from Polymer Solutions," ed by M. B. Huglin, Academic Press, London, 1972.*—Various features of the light scattering instruments are described systematically with the major purpose of helping investigators working on dilute polymer solutions to become acquainted with functions of important parts of the instrument. Emphasis has been placed on improving the versatility and performance of the existing light scattering photometers. The account is given in the following seven sections.

- I Introduction
- II Typical Light Scattering Instruments
- III Projecting Optical System
- IV Monitoring Optical System
- V Solution Cell and Temperature Control
- VI Receiving Optical System
- VII Detecting Electronic Design

Calibration and Correction Factors in Light Scattering from Polymer Solutions. H. Utiyama. *Chapter 4 in a monograph, "Light Scattering from Polymer Solutions," ed. by M. B. Huglin, Academic Press, London, 1972.*—Corrections required for measurements of the Rayleigh ratio in ordinary light scattering photometers are pointed out, and methods of quantitative estimation of the correction factors are described. Various methods of determination of calibration constant are also explained, and the characteristics of each method are discussed. The account is given in the following five sections.

- I Introduction
- II Correction Factors
 - Polarizer and Analyser, Scattering Angle, Transmittance of Neutral Filters, Corrections for Finite Beam Apertures of Incident and Scattered Lights, Corrections for Effects of Reflection.
- III Relationship between Final Light Scattering Results and Observable Quantities
 - Derivation of F and I' , Influence of Different Observable Quantities in Final Light Scattering Results.
- IV Determination of Calibration Constant
 - Use of Pure Liquids, Use of Low Molecular Weight Compounds, Use of Macromolecular Compounds, Use of Colloidal Dispersions.
- V Determination of Rayleigh Ratio with Absolute Light Scattering Photometer

Preparation and Physico-Chemical Properties of Highly Transparent and High Density Polyethylene Film from a Lightly Crosslinked Polyethylene.

H. Chu and Kitamaru. *Kobunshi Kagaku*, **29**, 323 (1972), in Japanese.—Completely transparent polyethylene (I) film has been made by compressing a melted sample of lightly crosslinked I prepared from linear I. The crystalline structure and physico-chemical properties of the film are examined by use of DSC and X-rays.

This sample not only has the same degree of crystallinity as the isotropically well-crystallized sample, but also shows abnormally high melting temperature such as 150–155°C. This film has also excellent mechanical properties as well as dimensional stability against heating.

The X-ray studies reveal that this sample has a characteristic crystalline structure, where P_{110} axis in reciprocal crystal lattice preferentially orients perpendicular to the film face.

Thermodynamic and Conformational Properties of Styrene—Methyl Methacrylate Block Copolymers in Dilute Solution. IV. Behavior of Diblock and Triblock Copolymers in Selective Solvents.

T. Kotaka, T. Tanaka and H. Inagaki. *Polymer Journal*, **3**, 327 (1972).—Solution properties of nearly equimolar AB-diblock and BAB-triblock copolymers, wherein A is polystyrene (PST) and B poly (methyl methacrylate) (PMMA), were examined in various selective solvents. In either type of selective solvents the diblock copolymers usually underwent *intermolecular association* and formed micelles, in which domains of PST- and PMMA-subchains were presumably segregated (*intramolecular phase separation*). The stability and size of such micelles depended on their molecular weight and composition as well as on the nature of solvents. The behavior of the triblock copolymers appeared to be more critically influenced by the solubility of the PMMA than that of the PST. In selective solvents having preferential solvency towards PMMA rather than PST, their behavior was more or less similar to that of the diblock copolymers whilst in selective solvents preferential to PST, they were usually unstable and liable to precipitate. In the transition region between the stable solution and precipitation states, the individual triblock copolymer chains often showed conformational anomalies without forming micelles, as shown by the intrinsic viscosity anomaly in *p*-xylene at 30°C. The possibility of *intramolecular association* of two PMMA subchains within a single triblock copolymer molecule was suggested as a hypothesis. However the hydrodynamic properties alone cannot provide decisive evidence for this possibility.

Thermodynamic and Conformational Properties of Styrene—Methyl Methacrylate Block Copolymers in Dilute Solution. V Light-Scattering Analysis of Conformational Anomalies in *p*-Xylene Solution.

T. Tanaka, T. Kotaka and H. Inagaki. *Polymer Journal*, **3**, 338 (1972).—Light-scattering studies were made in order to examine conformational anomalies exhibited by solution in *p*-xylene (*p*XY) of nearly equimolar AB-diblock and BAB-triblock copolymers, wherein A denotes polystyrene (PST) and B poly(methyl methacrylate) (PMMA). Particle-scattering function $P(\theta)$ was calculated on two simplified models: one is a micelle consisting of f molecules of AB-diblock type, of which B-subchains constitute the core

(star-shape model); and the other represents a BAB-triblock molecule, in which two side B-subchains undergo intramolecular association, forming a droplet, and the conformation of A-subchain is restricted by this droplet (arc-shape model). The calculated $P(\theta)$ functions were compared with the experimental data obtained in p XY solution at 30°C from AB-diblock and BAB-triblock samples. It was found that the star-shape model fits closely the behavior of the AB-diblock system; whilst the arc-shape model appears to give a reasonable description of the behavior of the BAB-triblock system (although the results are not completely conclusive).

Biochemistry

Fiber-Structured Material in a Fraction of *Bacillus Subtilis*. Y. Hiragi and H. Kadota. *J. Bacteriol.*, **108**, 579 (1971).—The paracrystal fractions of two species of *Bacillus* contain similarly structured fibrous material whose unit cell is hexagonal, with cell dimensions of $a=0.719$ nm and $c=0.963$ nm.

Tertiary Structure of Proteins. I. Representation and Computation of the Conformations. K. Nishikawa, T. Ooi, Y. Isogai and N. Saito. *J. Phys. Soc. Jap.*, **32**, 1331 (1972).—A protein conformation can be computed by connecting peptide units of usual trans-planar structure successively with a given set of dihedral angles φ and ψ . It is, however, not easy to generate the native conformations such as myoglobin and lysozyme by the computation. In order to show the discrepancy between the native conformation and the computed one, we have introduced a map, where the mutual distance between C α -atoms of i -th and j -th residue, r_{ij} , is listed against the residue number, in row and column. This map represents a tertiary structure of the protein (*e.g.* α -helix, β -structure) as the characteristic patterns. It becomes possible to estimate the difference of the computed conformation from the native one numerically by comparing the corresponding maps. The improvement of the dihedral angles, φ and ψ , as made by minimizing the deviation of the computed map from the native one on both myoglobin and lysozyme.

Tertiary Structure of Proteins. II. Freedom of Dihedral Angles and Energy Calculation. K. Nishikawa and T. Ooi. *J. Phys. Soc. Jap.*, **32**, 1338 (1972).—By using the procedure described in a preceding paper, several sets of φ and ψ are obtained which reproduced similar conformations to the native structure of lysozyme or myoglobin. Contrary to the expectation, the value of f has no maximum along a line connected any two of the minima in the $2n$ -dimensional phase space. This result shows the existence of many solutions for φ and ψ which generate the native conformation under restricted condition of fixed geometry in the main chain. Energy calculation is performed on the conformations obtained above to examine atomic collisions along the main chain. After refinement to remove the collisions, a conformation is finally obtained for lysozyme which has a total energy of -270 kcal/mol and still has a low value of f . Similarly a conformation can be found for myoglobin having an energy of -580 kcal/mol in total.

Rotational Freedom in Proline Residue. K. Nishikawa and T. Ooi. *Prog. Theor. Phys.*, **46**, 670 (1972).—Rotational freedom about N-C α bond in pyrrolidine ring of proline residue was considered in order to elucidate the flexibility of the ring. Energy computation showed that the distortion of the ring is allowed in the range of $\pm 20^\circ$ from the planar structure.

Termination of RNA Transcription on the Replicative Form DNA of Bacteriophage fd. M. Takanami, T. Okamoto and M. Sugiura. *J. Mol. Biol.*, **62**, 81 (1971).—In an RNA synthesizing system consisting of the doubly closed replicative form DNA of phage fd as template and purified *E. coli* RNA polymerase holo-enzyme, synthesis of RNA chains starting with pppA..... proceeded to a size corresponding to about one turn of the template and terminated at either low or high salt. Transcription of the (pppA.....) RNA chains was restricted to at least five different sites by adding the rho factor. The rho-induced termination at two of these sites was active at high salt, whereas the termination at the other sites functioned only at low salt. The termination at the rho-dependent sites would be influenced by the ionic environment in cells, resulting in the control of transcription.

Observations on the Structure of the Termination Factor Rho and its Attachment to DNA. T. Oda* and M. Takanami, (*Cancer Institute, Okayama University Medical School). *J. Mol. Biol.*, **71**, 150 (1972).—The termination factor "rho" appeared as a hexagonal arrangement of six subunits of identical size. The approximate diameters of the hexagonal particle and each subunit were 115 Å and 40 Å, respectively. On mixing with the replicative form DNA of phage fd, a limited number of the rho factor was seen attached to the circular DNA molecule, by setting the DNA strand in its empty core.

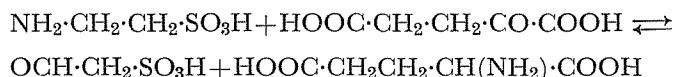
RNA Polymerase Binding Sites of Phage fd Replicative Form DNA. T. Okamoto, M. Sugiura and M. Takanami. *Nature New Biology*, **237**, 108 (1972), —The binding sites of RNA polymerase were isolated from phage fd replicative form DNA based on the finding that the DNA regions associated with RNA polymerase were protected from nucleolytic digestion. The average chain length of the isolated fragments was thirty-five base pairs long. Analysis of the nucleotide composition indicated an enrichment of the A-T content and double strandedness for the binding sites. The specificity of transcription was still retained in the isolated fragments.

Lysine Metabolism, and its Diversity and Enzymological Aspects. K. Soda and H. Misono. *Tanpakushitsu, Kakusan, Koso*, **17**, 42 (1972), in Japanese.—Metabolic pathways of lysine in mammals, avians, shells, and microorganisms were reviewed in detail from the viewpoint of comparative biochemistry and enzyme chemistry. In the section of mammalian lysine metabolism saccharopine pathway in which lysine is metabolized through saccharopine (ϵ -N-(L-glutaryl-2)-L-lysine), α -aminoadipic acid to yield glutaryl-CoA, was described, followed by the explanation of N-acetylation pathway in which ϵ -N-acetyllysine is a main intermediate, and homocitrulline pathway. Lysine is decomposed with *Glostridium* sp. via β -lysine and β -keto- δ -aminocaproic acid to butyrate, acetate and ammonia. Enzymological properties of lysine α , β -aminomutase and β , δ -diaminocaproic acid oxidoreductase were also mentioned. In aerobic

bacteria lysine is metabolized by lysine monooxygenase in *Pseudomonas fluorescens*, by lysine transaminase in *Achromobacter liquidum* and by N-acetyl transferase in *Aerobacter aerogenes*. The mechanism of the transaminase reaction was discussed to elucidate its properties and compare with the other pyridoxal phosphate enzymes.

Studies on Taurine- α -ketoglutarate Transaminase Reaction in Bacteria.

- S. Toyama and K. Soda. *Amino Acid and Nucleic Acid*, 24, 50 (1971), in Japanese.—1. The high activity of taurine- α -ketoglutarate transaminase was found exclusively in the cell-free extracts of *Achromobacter superficialis* and *Ach. polymorph*. The former was chosen for characterization of the enzymatic reaction.
2. The enzyme activity was enhanced inducibly by addition of β -alanine to the growth medium.
 3. The Product from α -ketoglutarate was identified as L-glutamate.
 4. Another product has been isolated, purified, and identified as sulfoacetaldehyde (2-oxoethanesulfonate), a deamination product from taurine, by comparison between the 2,4-dinitrophenylhydrazones of the synthetic and enzymatic products on the basis of studies by paper chromatography, visible, IR and NMR spectrophotometries, and elemental analysis.
 5. This enzymatic transamination was found to proceed stoichiometrically and reversibly as follows.



Preparation and Some Properties of Crystalline Kynureninase (*Pseudomonas marginalis*). M. Moriguchi, T. Yamamoto and K. Soda. *Amino Acid and Nucleic Acid*, 24, 75 (1971), in Japanese.—Kynureninase (L-kynurenine hydrolase EC 3.7.1.3) has been purified from the extract of *Pseudomonas marginalis* approximately 130-fold by a procedure including column chromatography on DEAE-cellulose, Sephadex G-150 and hydroxylapatite. The purified enzyme was crystallized by addition of ammonium sulfate. The crystalline enzyme is homogeneous by the criteria of ultracentrifugation and disc gel electrophoresis. The molecular weight is 100,000, assuming a partial specific volume of 0.74, and 1 mole of pyridoxal 5'-phosphate is bound per mole of enzyme as a coenzyme. The enzyme exhibits absorption maxima at 280, 337, and 430 $m\mu$. No appreciable spectral change is observed on varying pH. The coenzyme is resolved from the enzyme by the treatment with either hydroxylamine or L-alanine, followed by dialysis.

Studies on Bacterial Glutaminase: Purification and Characterization of Isozymes of Glutaminase from *Pseudomonas aeruginosa*. K. Soda, M. Ohshima and T. Yamamoto. *Amino Acid and Nucleic Acid*, 25, 87, (1972), in Japanese.—The Purification of glutaminase from the cell-free extract of *Pseudomonas aeruginosa*, and the occurrence of two isozymes are described. Glutaminase A is crystallized by addition of ammonium sulfate. Glutaminases A and B are homogeneous upon disc gel electrophoresis. Glutaminase A catalyzes the hydrolysis of L-glutamine, D-glutamine, L-asparagine, and D-asparagine, and also the formation of the hydrox-

amates from these substrates. The hydrolysis of L-glutamine, D-glutamine, L-theanine and D-theanine, and also the formation of the hydroxamates from these substrates are catalyzed by glutaminase B. L- γ -Glutamylhydrazine and L- γ -glutamyl-p-nitroanilide can be also the substrate for glutaminase B.

Purification and Crystallization of Taurine: α -Ketoglutarate Transaminase from *Achromobacter superficialis*. S. Toyama, H. Misono and K. Soda. *Amino Acid and Nucleic Acid*, **25**, 91 (1972), in Japanese.—The preparation and some properties of crystalline taurine: α -ketoglutarate transaminase from *Achromobacter superficialis* is described. The Enzyme was purified approximately 65-fold from the cell-free extract of *Ach. superficialis* by DEAE-cellulose column chromatography, ammonium sulfate fractionation, hydroxyl apatite and Sephadex G-150 column chromatography, and crystallized by addition of ammonium sulfate. The enzyme exhibits absorption maxima at 280 and 340 m μ . No appreciable spectral change was observed on varying pH. The enzyme is homogeneous by the criteria of ultracentrifugation and disc gel electrophoresis. The molecular weight is 156,000, and four moles of a vitamin B₆ compound are bound per mole of the enzyme. The enzyme catalyzes the transamination of DL- β -aminoisobutyrate, β -alanine, taurine, and 3-aminopropanesulfonate to α -ketoglutarate. The enzyme inactivated by treatments with ammonium sulfate is activated by incubation with pyridoxal 5'-phosphate at 40~60°C for about 10 min.

Crystalline Kynureninase from *Pseudomonas marginalis*. M. Moriguchi, T. Yamamoto and K. Soda. *Biochem. Biophys. Res. Commu.*, **44**, 752 (1971).—The preparation of crystalline kynureninase from *Pseudomonas marginalis* is described. The enzyme is homogeneous by the criteria of ultracentrifugation and disc gel electrophoresis. The molecular weight is 100,000 and 1 mole of pyridoxal 5'-phosphate is bound per mole of enzyme as a coenzyme. The enzyme exhibits absorption maxima at 280, 337 and 430 m μ . The coenzyme is resolved from the enzyme by the treatment with hydroxylamine or L-alanine.

Crystalline L-Leucine Dehydrogenase. K. Soda, H. Misono, K. Mori and H. Sakato. *Biochem. Biophys. Res. Commu.*, **44**, 931 (1971).—The preparation of crystalline L-leucine dehydrogenase from the extract of *Bacillus sphaericus* is described. The enzyme is homogeneous by the criteria of ultracentrifugation and disc gel electrophoresis. The molecular weight is 280,000. The enzyme catalyzes the oxidative deamination of L-leucine, L-valine, L-isoleucine, L-norleucine and L-norvaline, while none of D-leucine, D-valine, L-alanine and L-glutamate is deaminated. NAD only serves as the hydrogen acceptor.

Inactivation of Kynureninase by L-alanine. M. Moriguchi, T. Yamamoto and K. Soda. *Biochem. Biophys. Res. Commu.*, **44**, 1416 (1971).—Kynureninase is inactivated by incubation with a reaction product, L-alanine. The activity is restored by addition of pyridoxal 5'-phosphate. Addition of L-alanine to the enzyme causes a decrease in absorbance at 430 m μ , and appearance of a peak at 325 m μ . The inactivated enzyme is resistant to a borohydride reduction. The result suggest

occurrence of the enzymatic transamination of the coenzyme moiety with L-alanine to inactivate the enzyme.

Purification and Properties of Isozymes of Glutaminase from *Pseudomonas aeruginosa*. K. Soda, M. Ohshima and T. Yamamoto. *Biochem. Biophys. Res. Commu.*, **46**, 1278 (1972).—The purification of glutaminase from the cell-free extract of *Pseudomonas aeruginosa*, and the occurrence of two isozymes are described. Glutaminase A is crystallized by addition of ammonium sulfate. Glutaminases A and B are homogeneous upon ultracentrifugation and disc gel electrophoresis. Glutaminase A catalyzes the hydrolysis of L-glutamine, D-glutamine, L-asparagine and D-asparagine, and also the formation of the hydroxamates from these substrates. The hydrolysis of L-glutamine, D-glutamine, L-theanine and D-theanine, and also the formation of the hydroxamates from these substrates are catalyzed by glutaminase B. L- γ -Glutamylhydrazine and L- γ -glutamyl-*p*-nitroanilide can be also the substrates for glutaminase B.

Crystalline Taurine: α -Ketoglutarate Aminotransferase from *Achromobacter superficialis*. S. Toyama, H. Misono and K. Soda. *Biochem. Biophys. Res. Commu.*, **46**, 1374 (1972).—The preparation and some properties of crystalline taurine: α -ketoglutarate aminotransferase from *Achromobacter superficialis* is described. The enzyme exhibits absorption maxima at 280 and 340 m μ . No appreciable spectral change was observed on varying pH. The enzyme is homogeneous by the criteria of ultracentrifugation and disc gel electrophoresis. The molecular weight is 156,000, and four moles of a vitamin B₆ compound are bound per mole of the enzyme. The enzyme catalyzes the transamination of DL- β -aminoisobutyrate, β -alanine, taurine, and 3-aminopropanesulfonate to α -ketoglutarate. The enzyme inactivated by treatments with ammonium sulfate is activated by incubation with pyridoxal 5'-phosphate at 45–60° for about 10 min.

Occurrence of Taurine: α -Ketoglutarate Aminotransferase in Bacterial Extracts. S. Toyama and K. Soda. *J. Bacteriol.*, **109**, 533, (1972).—High activity of taurine: α -ketoglutarate aminotransferase was found exclusively in cell-free extracts of *Achromobacter superficialis* and *A. polymorph*.

The former was chosen for characterization of the enzymatic reaction. The enzyme activity was enhanced by addition of β -alanine to the growth medium. The product from α -ketoglutarate was identified as L-glutamate. Another product has been isolated, purified, and identified as sulfoacetaldehyde (2-oxoethanesulfonate), a deamination product from taurine, by comparison between the 2,4-dinitrophenylhydrazones of the synthetic and enzymatic products on the basis of studies by paper chromatography, by visible, infrared, and nuclear magnetic resonance spectrophotometries, and by elemental analysis. This enzymatic transamination was found to proceed stoichiometrically and reversibly as follows: $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H} + \text{HOOC}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOH} \rightleftharpoons \text{OHC}\cdot\text{CH}_2\cdot\text{SO}_3\text{H} + \text{HOOC}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH}$.

Arginine Racemase of *Pseudomonas graveolens*. I. Purification, Crystallization, and Properties. T. Yorifuji, K. Ogata and K. Soda. *J. Biol. Chem.*, **246**,

5085, (1971).—Arginine racemase has been purified approximately 5400-fold and crystallized from an extract of *Pseudomonas graveolens*. The purification procedure consists of sonic disruption, ammonium sulfate fractionation, treatment with 1-butanol, DEAE-cellulose and DEAE-Sephadex column chromatography, and Sephadex G-150 gel filtration, followed by crystallization. The purified enzyme is homogeneous by the criteria of ultracentrifugation ($S_{20,w}^0=5.2$ S) and disc gel electrophoresis. The molecular weight is 167,000, assuming a partial specific volume of 0.74.

The enzyme is yellow in solution and exhibits an absorption maximum at 420 m μ . The absorption spectrum is shifted neither by varying pH of the enzyme nor by addition of arginine. One mole of pyridoxal 5'-phosphate is tightly bound per 42,000 g of enzyme. The apoenzyme was obtained by dialysis against phenylhydrazine solution. Addition of pyridoxal 5'-phosphate caused return of the 420 m μ absorption peak and reconstitution of activity. Reduction of arginine racemase with sodium borohydride shifted the 420 m μ peak to about 315 m μ , and destroyed the racemase activity. The enzyme catalyzes racemization of lysine, arginine, ϵ -N-acetyllysine, ornithine, 2,3-diaminopropionate, homoarginine, 2,4-diaminobutyrate, ethionone, citrulline, homocitrulline, δ -N-acetylornithine, theanine, glutamine, and methionine in this order, when examined at pH 10.0. Maximum activities for arginine, lysine, theanine, and ornithine are found in the pH regions of 9.0 to 10.6, 7.5 to 10.6, 7.0 to 10.0, and 6.5 to 9.0, respectively. The following Michaelis constants were determined: D-arginine, 1.0×10^{-3} M, and pyridoxal 5'-phosphate, 4.0×10^{-7} M. The enzyme activity was inhibited by hydroxylamine and D- and L-penicillamine.

Arginine Racemase of *Pseudomonas graveolens* Part II. Racemization and Transamination of Ornithine Catalyzed by Arginine Racemase.

T. Yorifuji, H. Misono and K. Soda. *J. Biol. Chem.*, **246**, 5093, (1971).—Arginine racemase from *Pseudomonas graveolens* is inactivated by preliminary incubation with L- or D-ornithine, δ -N-acetyl-L-ornithine, and L-2,4-diaminobutyrate at pH 10.0. Loss of the enzyme activity is associated with formation of a new spectrum with an absorption maximum in the region of 320 m μ and disappearance of a peak at 420 m μ . The inactivation is prevented, and the inactivated enzyme is reactivated by addition of pyruvate or oxaloacetate. Addition of pyridoxal 5'-phosphate has substantially no effect. Exhaustive dialysis of the enzyme treated with ornithine leads to loss of the absorption at about 320 m μ to yield apoenzyme. The apoenzyme is reactivated by adding either pyridoxal 5'-phosphate alone or pyridoxamine 5'-phosphate plus pyruvate. Inactivation appears to be due to formation of bound pyridoxamine 5'-phosphate from bound pyridoxal 5'-phosphate by transamination with ornithine, which is converted into Δ^1 -pyrroline-2-carboxylic acid, the intramolecularly dehydrated form of α -keto- δ -aminovaleric acid. Pyridoxamine 5'-phosphate formed is tightly bound to the protein moiety and dissociates from the enzyme only after long dialysis.

The enzyme catalyzes transamination between L- or D-ornithine (or certain other amino acids) and pyruvate (or certain other α -keto acids). There is correlation between the amino acids that cause inactivation and those that transaminate, and between the α -keto acids that reactivate the inactivated enzyme and those that transaminate. The rate of transamination is very low as compared to that of racemization.

The enzyme exhibits optimal activity at about pH 11 for transamination. The racemase is only slightly inactivated by incubation with ornithine in the lower pH region in which the rate of transamination is low.